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Infrared and infrared emission spectroscopy of the zinc carbonate mineral smithsonite

Ray L. Frost*, Wayde N. Martens, Daria L. Wain, Matt C. Hales

Inorganic Materials Research Program, School of Physical and Chemical Sciences, Queensland University of Technology, GPO Box 2434, Brisbane, Queensland 4001, Australia

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Abstract

Infrared emission and infrared spectroscopy has been used to study a series of selected natural smithsonites from different origins. An intense broad infrared band at 1440 cm⁻¹ is assigned to the ν_3 CO₃²⁻ antisymmetric stretching vibration. An additional band is resolved at 1335 cm⁻¹. An intense sharp Raman band at 1092 cm⁻¹ is assigned to the CO₃²⁻ symmetric stretching vibration. Infrared emission spectra show a broad antisymmetric band at 1442 cm⁻¹ shifting to lower wavenumbers with thermal treatment. A band observed at 870 cm⁻¹ with a band of lesser intensity at 842 cm⁻¹ shifts to higher wavenumbers upon thermal treatment and is observed at 865 cm⁻¹ at 400 °C and is assigned to the CO₃²⁻ ν_2 mode. No ν_2 bending modes are observed in the Raman spectra for smithsonite. The band at 746 cm⁻¹ shifts to 743 cm⁻¹ at 400 °C and is attributed to the CO₃²⁻ ν_4 in phase bending modes. Two infrared bands at 744 and around 729 cm⁻¹ are assigned to the ν_4 in phase bending mode. Multiple bands may be attributed to the structural distortion ZnO₆ octahedron. This structural distortion is brought about by the substitution of Zn by some other cation. A number of bands at 2499, 2597, 2858, 2954 and 2991 cm⁻¹ in both the IE and infrared spectra are attributed to combination bands. © 2007 Elsevier B.V. All rights reserved.

Keywords: Aurichaclite; Hydrozincite; Smithsonite; Rosasite; Hydroxy carbonates; Infrared and Raman spectroscopy; Infrared emission spectroscopy

1. Introduction

Smithsonite is a secondary mineral of zinc formed in the oxidation zone of zinc bearing ore bodies hexagonal with point group 3 bar 2/m. The mineral is named for James Smithson, the founder of the Smithsonian Institution (USA). The mineral is renowned for its pearly lustre and comes in a range of colours which vary across all colours of the visible spectrum. Although it must be stated that no studies have been undertaken to explain the colours of smithsonite even though some chemical analyses of the coloured smithsonites have been undertaken. It is interesting that some chemical analyses of smithsonites from different origins was first published in 1898 by W.O. Crosby. Carbonates with intermediate sized divalent cations normally crystallise in the calcite structure [1]. Those with larger cations have an aragonite type structure.

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Of the secondary minerals of zinc only two minerals are known namely smithsonite and hydrozincite. The formation of these minerals is controlled by the partial pressure of CO_2 [2,3]. According to the equation for the formation of hydrozincite 5ZnO (s) + 2CO₂ (g) \leftrightarrow Zn₅(CO₃)₂(OH)₆ (s) with log K = 10.32 [2]. Thus ZnO is unstable with respect to hydrozincite at partial pressures above $10^{-5.16}$. If the partial pressure of CO₂ increases above $10^{-1.41}$ smithsonite formation is favoured according to the reaction $Zn_5(CO_3)_2(OH)_6$ (s) + 3CO₂ (g) \leftrightarrow 5ZnCO₃ $(s) + 3H_2O(g)$. These results provide implications for the relative stability of hydrozincite and smithsonite. It is noted that hydrozincite may form from solutions resulting from the oxidized zone of a Pb-Zn ore body [2]. Thus zincite (ZnO) is a rare mineral and smithsonite is only stable at elevated CO₂ partial pressures. The partial pressure range for the stability of hydrozincite according to Williams is limited and no doubt this accounts for the scarcity of the mineral in nature [3]. The mineral can be readily synthesised in the laboratory and is often found in corrosion products of zinc [4–6].

The free ion, CO_3^{2-} with D_{3h} symmetry exhibits four normal vibrational modes; a symmetric stretching vibration (v_2),

^{*} Corresponding author. Tel.: +61 7 3138 2407; fax: +61 7 3138 1804. *E-mail address:* r.frost@qut.edu.au (R.L. Frost).

Table 1			
Table of the infrared	spectra	of selected	smithsonites

Cente WHM % Area WHM % Area Cente WHM % Area Cente WHM % Area Cente WHM % Area K <th colspan="2">Smithsonite (New Mexico, aqua green)</th> <th colspan="2">Cadmian smithsonite (S. Ireland, yellow)</th> <th colspan="2">Smithsonite (Namibia, light pink)</th> <th colspan="3">Smithsonite (Mexico, clear rose pink)</th> <th>Smithso light gre</th> <th colspan="3">Smithsonite (Namibia, light green)</th> <th colspan="3">Smithsonite (Namibia, clear)</th>	Smithsonite (New Mexico, aqua green)		Cadmian smithsonite (S. Ireland, yellow)		Smithsonite (Namibia, light pink)		Smithsonite (Mexico, clear rose pink)			Smithso light gre	Smithsonite (Namibia, light green)			Smithsonite (Namibia, clear)				
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$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	3330	251.7	3.45															
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236 64.6 0.50 1813 31.0 0.33 1812 24.6 0.5 1807 19.0 0.26 1813 27.2 0.55 1813 27.2 0.55 1509 53.3 0.20 1848 100.9 10.41 1487 96.3 13.59 1486 88.3 12.23 1483 95.6 16.44 1491 94.2 13.01 1400 127.9 16.3 129.9 26.35 1412 1436 129.9 26.35 1412 1436 129.9 26.35 1412 1436 129.9 26.35 1412 1436 129.9 26.35 1418 95.5 27.37 1418 95.5 23.59 1412 37.5 23.59 145 140 129.9 26.35 1418 95.5 21.99 185.5 25.98 159.7 21.59 159.7 21.5 159.7 21.5 159.7 21.5 159.7 21.5 159.7 21.5 159.7 21.5 159.7 21.5 159.7 21.5 159.7 21.5 159.7 21.5 159.	2363	17.0	0.11															
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$ \begin{array}{cccccccccccccccccccccccccccccccccccc$																1509	53.3	2.01
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$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	1412	71.9	10.61	1416	82.3	17.40	1420	85.3	25.62	1418	85.2	27.37	1418	93.5	23.59	1418	37.5	2.08
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$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$										1240	227.9	21.93	1222	207.9	19.79			
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$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	1045	112.8	2.56	1037	173.1	2.51				1051	159.7	2.15	1046	160.4	2.43			
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	961	73.0	1.01							946	47.4	0.90						
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	872	12.4	1.02	874	10.3	0.75	873	12.0	1.72	874	10.4	0.92	873	14.4	1.32	874	11.4	1.27
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$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	811	56.6	1.64	807	39.2	1.13	799	48.1	1.06	795	42.2	0.75	812	51.5	1.22	802	49.6	1.10
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729 18.8 0.50 727 20.1 0.67 732 14.0 0.48 731 16.0 0.50 729 14.9 0.58 730 16.3 0.49 712 34.6 0.58 707 25.6 0.61 719 25.3 0.64 717 25.7 0.48 712 33.3 0.55 714 32.6 0.59 676 70.2 0.38 683 67.9 0.38	738	10.9	0.48	738	11.1	0.58	739	8.8	0.52	739	9.9	0.53	738	8.1	0.30	739	9.8	0.54
712 34.6 0.58 707 25.6 0.61 719 25.3 0.64 717 25.7 0.48 712 33.3 0.55 714 32.6 0.59 676 70.2 0.38 683 67.9 0.38 0.45 690 48.6 0.33 677 13.5 0.22 684 64.0 0.34	729	18.8	0.50	727	20.1	0.67	732	14.0	0.48	731	16.0	0.50	729	14.9	0.58	730	16.3	0.49
676 70.2 0.38 683 67.9 0.38 693 32.9 0.45 690 48.6 0.33 676 70.2 0.38 683 67.9 0.38 677 13.5 0.22 684 64.0 0.34	712	34.6	0.58	707	25.6	0.61	719	25.3	0.64	717	25.7	0.48	712	33.3	0.55	714	32.6	0.59
676 70.2 0.38 683 67.9 0.38 677 13.5 0.22 684 64.0 0.34 525 0.0 4.47							693	32.9	0.45	690	48.6	0.33						
525 0.0 4.47	676	70.2	0.38	683	67.9	0.38							677	13.5	0.22	684	64.0	0.34
													525	0.0	4.47			

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